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ULTRADISPERSE BATCH FOR LOW-ALKALI ALUMINOBOROSILICATE GLASSES

N. F. Zhernovaya,[1,2] I. V. Tret'yakov,[1] and F. E. Zhernovoi[1]

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It is determined that ultradisperse activated batches obtained by wet milling in a planetary mill are effective for synthesizing low-alkaline borosilicate glasses (Pyrex type). The positive effect is attained, first and foremost, by intensifying the stages of glass formation — dissolution of free silica. The glassmaking temperature can be lowered by 100 – 150°C.

Key words: low-alkali borosilicate glass, batch, wet milling, activation, melting, efficacy.

The duration, energy intensiveness and particulars of glassmaking are largely determined by the composition and state of the actual batch used [1]. Numerous scientific studies devoted to perfecting and activating glass batches, first and foremost, refractory-glass batches which are difficult to melt thoroughly, fully confirm the importance and reliability of this classical rule in glassmaking technology.

The present work is devoted to studying refractory batches of low-alkali, Pyrex-type, borosilicate glasses, widely used in different areas of the national economy, science and engineering (the chemical industry, pharmaceuticals, medicine, computing and computer engineering, communications, construction and elsewere) owing to a complex of extremely valuable physical-chemical and mechanical characteristics.

The experimental batches (Table 1) for the model glass composition (wt.%) — 81 SiO_2, 12 B_2O_3, 2 Al_2O_3, and 5 Na_2O — were calculated using alternative boron-containing (boric acid, Borax) and aluminum-containing (alumina, perlite) raw materials (Table 2).

The Fogel–Fulcher–Tamman (FFT) equation obtained for the temperature dependence $\log \eta = f(t)$ of the viscosity of Pyrex glass (initial data: working temperature 1270°C, $\log \eta = 3$, Littleton temperature 820°C, $\log \eta = 6.6$; annealing temperature 560°C; $\log \eta = 12$ [2])

$$\log \eta = -2.64 + \frac{6511.5}{t - 115.2}$$

confirms the refractory nature of this composition: the melting interval ($\log \eta = 2 - 1$) corresponds to temperatures from 1520 to 1700°C and above (Fig. 1).

A particularity of the batch melting process for low-alkali borosilicate glasses manifests in the fact that no more than 20 wt.% of the silicon dioxide enters into the silicate formation reaction while 80 wt.% of the free quartz grains should dissolve in the primary melt formed (for comparison, in sodium-calcium-silicate glasses, such as sheet and container glass, the amount of silica not bound in silicates does not exceed 25%). In high-viscosity melt, the diffusion-li-

[1] V. G. Shukhov Belgorod State Technological University, Belgorod, Russia.
[2] E-mail: natalia.zhernovaya@gmail.com.

TABLE 1. Experimental Batch Compositions

Batch	Mass parts (per 100 mass parts of batch)							Glass yield, %	Batch melting loss, %
	Sand	Boric Acid	Borax	Alumina	Perlite	Soda	Σ		
1	81.38	21.38	–	1.94	–	8.61	113.31	88.25	11.75
2	75.08	5.57	24.35	–	9.53	–	114.53	87.31	12.69
3*	85.66	–	34.66	2.04	–	–	122.36	81.73	18.27

* The Na_2O mass fraction is 5.3% in batch-3 based glass.

TABLE 2. Chemical Composition of Raw Materials

Material	Content, wt.%				
	SiO_2	B_2O_3	Al_2O_3	Na_2O	Fe_2O_3
Sand	99.5	–	0.1	–	0.04
Boric acid	–	56.1	–	–	–
Technical 10-H_2O borax	–	36.4	–	16.2	–
Alumina	0.5	–	98.8	0.6	0.1
Perlite	70.4	–	14.7	6.0	1.1
Calcined, technical soda	–	–	–	58.0	0.003

mited quartz dissolution process is extremely slow and prolonged. High viscosity greatly complicates fining and homogenization of the molten glass. As a result the glass-making process for glasses of the type indicated is greatly impeded [3, 4].

A direct-fired, gas-flame, regenerative furnace with air heated to 800°C is commonly used in the production of low-alkali borosilicate glasses. Flue gases, flowing in the opposite direction toward the loading arch, are discharged through cylindrical ceramic and metal recuperators into the stack. Electric heating (molybdenum electrodes) was installed into the glassmaking furnace both to intensify the process and as a barrier. The molten glass slowly moves in the furnace, being constantly drawn into different vertical and horizontal flows, and is gradually homogenized. The temperature is 1200°C in the loading section of the furnace and higher than 1650°C in the fining section. The total time from feeding batch into the furnace to formation of glass parts ranges on average from 2 to 3 days [5].

On the basis of these factors it was proposed that special processing — fine wet milling — be used to intensify melting of borosilicate glass batches:

– ultradisperse, hydrated, quartz-sand particles are much lighter and dissolve more quickly in the primary silicate melt;

– water increases the efficiency of batch milling and eliminates adsorption of air on the surface of the particles.

Wet comminution of glass batches (see Table 1) was performed in the SAND laboratory centrifugal-planetary mill (batch : water = 2 : 1, drum volume 0.37 liters, maximum rotation rate 325 sec^{-1}) for 0.5 h followed by pouring the suspension into a mold and drying under natural conditions and in a drying oven at 100 – 110°C.

The main parameters affecting the milling efficiency are:

– drum rotation rate around the central axis, determining the acceleration of the centrifugal field, which is ten times greater than the acceleration of gravity;

– ratio of the rotation rates of the drum around its own and the central axes, forming the method by which the milling bodies act on the material (impact, abrasion, mixed).

Analysis of the suspensions obtained, performed in a Microsizer 201 laser analyzer, showed that more than 90% of the particles were smaller than 20 μm and 40% were smaller than 5 μm with the following differential distribution (Fig. 2).

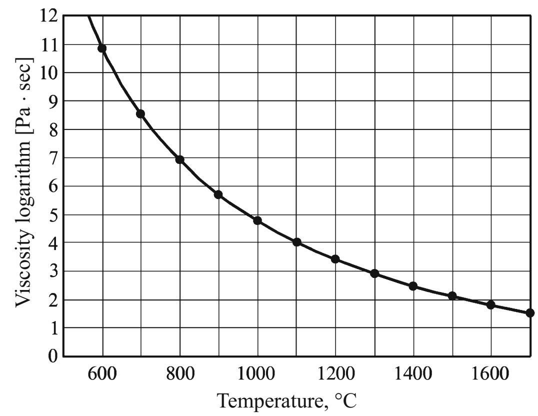

Fig. 1. Temperature dependence of the viscosity of Pyrex glass.

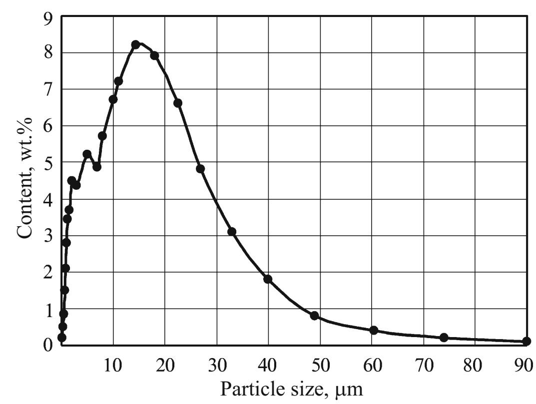

Fig. 2. Differential particle distribution curve of the batch suspension.

a

b

Fig. 3. Briquettes of ultradisperse batches after drying: *a*) under natural conditions; *b*) at temperature 100 – 110°C.

The dried ultradisperse batches (UDB) comprised conglomerates (Fig. 3); in addition, drying at elevated temperatures resulted in their compaction and hardening (Table 3).

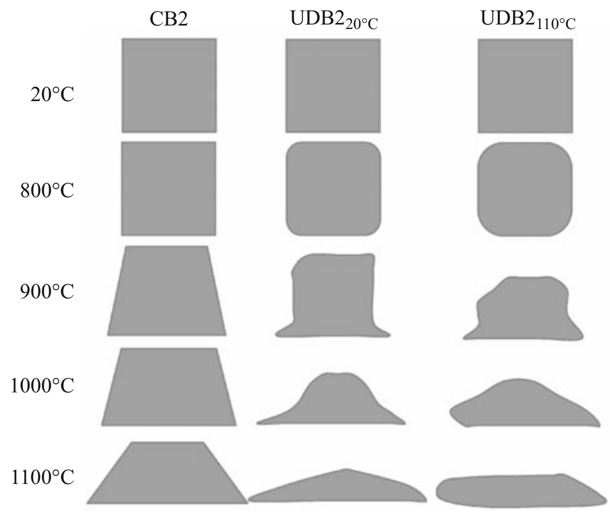

Fig. 4. Schematic diagram of batch 2 during polythermal heat-treatment.

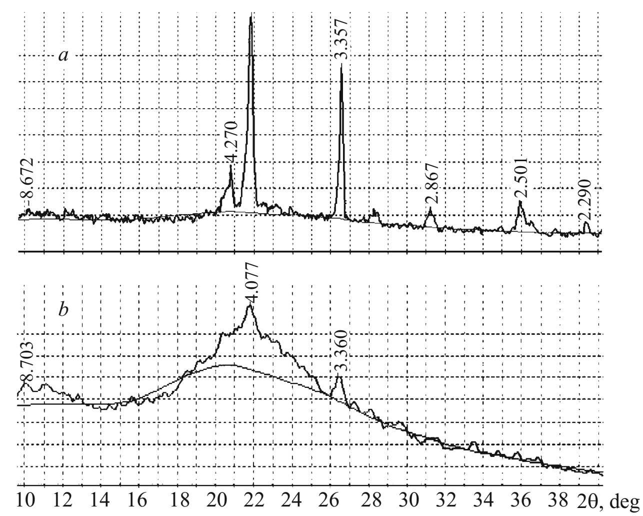

Fig. 6. Diffraction patterns of the products of heat-treatment at 1300°C of the batches CB2 (*a*) and UDB2$_{20°C}$ (*b*).

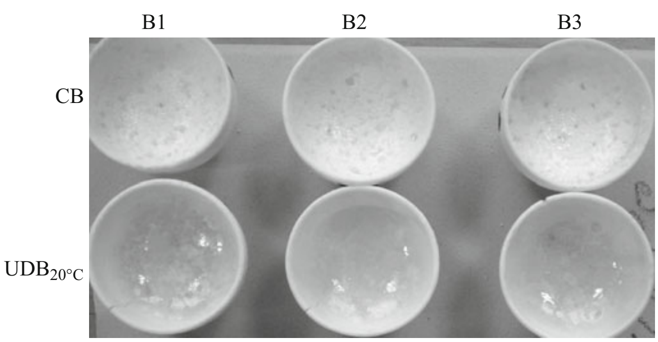

Fig. 5. Products of heat-treatment at 1300°C of conventional and ultradisperse batches.

A comparative study of the glassmaking process was done by stepped heat-treatment of loose conventional batches (CB) and briquetted ultradisperse batches (UDB) from 700 to 1100°C every 100°C followed by visual and thermogravimetric checking and x-ray phase analysis of the sintered masses.

Ultradisperse batches dried under natural conditions (UDB$_{20°C}$) and in a drying furnace (UDB$_{110°C}$) started to melt at 800°C; significant volume shrinkage (about 25 – 30%) resulting from intense sintering with the participation of a liquid phase was observed at 900°C, after which masses whose surface was coated with a glassy film gradually collapsed and spread. In a conventional batch, starting at 900°C small volume shrinkage was observed, the cylindrical briquettes became conical and gradually collapsed (Fig. 4).

Heat-treatment for 1 h at 1300°C resulted in completion of glass formation in ultradisperse batches, while conventional batches only sintered and foamed (Fig. 5).

XPA showed that wet milling and mechanical activation of the batches promote cristobalitization of quartz grains, because numerous micro-cracks and non-equilibrium defects form in them [6], as well as their subsequent intense dissolution. There are virtually no crystalline phases in the products of heat-treatment of ultradisperse batches (1300°C), i.e., it can be assumed that glass formation was practically completed in them. At the same time a large amount of a crystalline phase in the form of insoluble quartz grains and cristobalite with a very small fraction of glass phase is found in conventional batch (Fig. 6).

The synthesis of the model glasses performed in a laboratory electric furnace at 1450°C confirmed the efficacy of ultradisperse batch obtained by wet milling. The differences between products obtained from conventional and ultradisperse batches are quite clearly seen in Fig. 7.

Glasses were obtained at moderate synthesis temperature from ultradisperse batches. The glasses contain a significant

TABLE 3. Properties of UDB Briquettes

Indicator	UDB 1		UDB 2		UDB 3	
	Drying temperature, °C					
	20	110	20	110	20	110
Density, kg/m^3	1376.9	1474.1	1130.3	1264.3	1207.4	1268.5
Compression strength, MPa	0.72	2.39	0.43	1.58	0.26	2.86

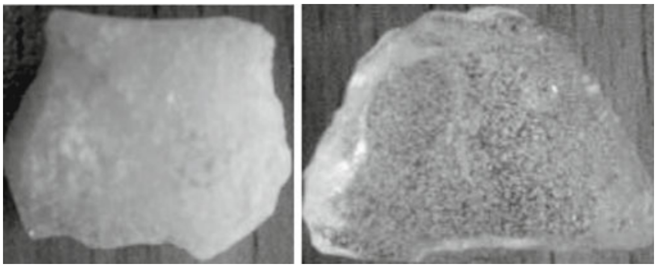

Fig. 7. Products of synthesis at 1450°C of model glasses.

number of fine bubbles, which can be explained by the absence of convective motion of the molten glass during melting in a crucible and fining agents in the batch. Glass formation in conventional batch is far from complete: the primary melt contains a large number of undissolved quartz grains and cristobalite, which can be seen visually, under a microscope and by x-ray diffraction.

The advantage of using natural perlite, an effusive amorphous rock characterized by a high-energy state, in the batches was discovered in the course of the experimental work. The only limitation of using perlite is that it contains a large amount of iron oxides (see Table 2).

Checking the physical-chemical properties of the glasses synthesized from UDB (density 2290 kg/m^3, refractive index 1.480, water-resistance 0.15 ml/g, 1st hydrolytic class under exposure to 0.01 N HCl) confirmed that their chemical compositions corresponded completely to the model composition of the glass.

In summary, it has been shown that the development of a technology together with using mechanically activated wet-milled batches is a promising direction for low-alkali alumino-borate glasses. The efficacy of domestically produced, continuous action, planetary mills [7] as well as the small-scale production of this type of glass make the commercial realization of the technology very likely.

The use of UDB will make it possible to lower the glassmaking temperature by 100 – 150°C, do away with adding to the batch NaCl glassmaking accelerators, extend the furnace run, and improve the environmental conditions of production.

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